Trace Metal Analysis of Waters using the Carbon Rod Atomizer — a Review

Application Note

Atomic Absorption

Author

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Environmental scientists are demanding more of the analytical chemist in their quest to understand the complex relationships existing between trace metals and living organisms. Current water studies are being directed towards the determination and distribution of the various physico-chemical forms of trace metals in natural and waste waters. A trace metal's chemical form and properties will be determined by its interaction with the parent matrix. Environmental water samples are extremely variable in their composition, and information about their origin (whether sea, lake, river or sewage) is essential in determining the approach and techniques used in an analysis. Invariably the analysis will involve the determination of either total metal or trace constituent. The total metal constituent is an absolute value which considered solely may not often reflect the biological or environmental activity of a particular constituent. However, if the total constituent is considered in conjunction with other total constituents, its role in a particular water sample may become apparent. It is therefore essential that the total trace metal be determined accurately and precisely.

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Direct Analysis of Water Samples

The United States Environment Protection Agency (USEPA) determine very low levels of trace metals in water samples by direct injection onto the carbon rod atomizer. The samples are treated to give four physico-chemical forms of the metal [1].

• Dissolved Metals: Those constituents (metals) which will pass through a 0.45 μm membrane filter.

• Suspended Metals: Those constituents (metals) which will be retained by a 0.4 μm membrane filter.

• Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion, or the sum of the concentrations of metals in both the dissolved and suspended fractions.

• Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid.

After treatment, the sample is injected onto the graphite tube, dried, ashed and atomized. In the treatment of sea water samples, contamination from reagents, filters, glassware and storage containers can play a significant role in obtaining an accurate result.

Interferences in Sea Water Analysis

The oceans are being used for the deposition of environmental wastes and therefore a great deal of attention has been given to the analysis of trace elements in sea water. Sea water is a challenging matrix for the analytical chemist due to the very low concentrations [2,3] of many important trace metals. Furthermore, the high salt content, mainly sodium chloride, can cause substantial background and chemical interferences in flameless atomic absorption. Two approaches in the elimination and reduction of interferences due to the high content of alkali chlorides have been prevalent in recent studies using the carbon rod. These are:

• Separation and preconcentration of trace metals from the sea water matrix.

• Modification of the sea water matrix to eliminate the effect of chloride by converting the metal chloride to another form thus altering the atomization properties of the analyte and interfering halide salts.

Separation and preconcentration is time consuming and prone to contamination but permits a greater analytical range. The matrix modification method is fast, and requires little sample preparation with the modifying agent and is often applied directly to the sample on the carbon rod atomizer.

Separation and Preconcentration of Trace Metals in Sea Water

Furnace atomization is a very sensitive technique. Often the limiting factor to meaningful and accurate data is the degree of care taken with the sample collection and analytical procedures employed prior to determination on the carbon rod atomizer. When separation and preconcentration methods are employed in the analysis of trace metals, errors resulting from incomplete sampling digestion, and contamination arising from reagents, storage containers, glassware and incorrect storage procedures can be significant. The most popular methods presently being used for the determination of trace metals in water are solvent extraction and ion exchange.

Bruland, Franks, Knauer and Martin have investigated the sampling and preconcentration of copper, cadmium, zinc, and nickel from sea water [4].

The sea water sample was doubly extracted into chloroform at pH4 using an ammonium acetate buffer and an ammonium pyrolidinedithiocarbamate (APCD) and diethylammonium diethyldithiocarbamate (DDC) mixed chelate system [5]. The extract was then back extracted into nitric acid which was evaporated to dryness and redissolved in a smaller volume of nitric acid to give a concentration factor of 200:1. Metal recoveries were in excess of 99%. Chelex 100 was also used to preconcentrate the metals and these results and recoveries were compared with the solvent extraction method. The Chelex 100 technique was found to remove only 60% of the copper in sea water concurring with other studies [7]. Quartz-distilled reagents were employed and sampling vessels were carefully cleaned. The solvent extraction procedure does not differ greatly from other analysis systems used [5-7] for the determination of Cr, V, Fe, Co, Ni, Mo and Pb in sea and natural waters. The use of the back extraction allows the determination of Mn whose extracted complex has been found to decompose almost immediately on entering the organic phase [6]. In the determination of total Cr it is essential that all Cr species are oxidized to the extractable hexavalent form [8] before extraction with the carbamate.

Matrix Modification

During the atomization process many species can be formed, each having a characteristic volatility and molecular absorption spectrum. Molecular absorption can therefore result in high background absorption signals coincident with the atomic absorption signal. Such high background absorption signals should be reduced or eliminated to improve the accu-

racy of the AA measurement. Culver and Surles [9] investigated the absorption spectra during atomization of the following alkali metal salts: NaF, NaCl, KCl, KBr, NaI, $CaCl_2$, Na_2SO_4, $NaNO_3$ and Na_2HPO_4 over the range 200–400 nm on the CRA–63. Substantial molecular absorption was observed for the alkali halides while the oxy-anions showed little absorption with weak bands for nitrate and sulphate being observed at 220 nm.

Recent studies indicate that the conversion of the alkali halides to their alkali oxy-anion salts leads to reduced molecular spectra and a more volatile salt which can be ashed at a lower temperature [10,11,12].

The spectra and effects on the atomization peaks of analytes and various chemical matrix modifiers can now be observed on laboratory atomic absorption instruments which have a CRT display. On an instrument such as the AA-875 it is possible to follow the background absorption peak as well as the atomic absorption of the analyte. For greater accuracy and precision the complete resolution of the background and analyte atomization peaks is required; this can be achieved by matrix modifiers. In recent studies involving the characterization of atomization peaks two analytical parameters were introduced [10,13]. These are the "appearance atomization temperature" and the "peak atomization temperature".

The "appearance atomization temperature" is defined as the first appearance of the atomic absorption signal above the noise which is equivalent to twice the standard deviation of the baseline [12].

The "peak atomization temperature" is defined as the temperature of maximum absorbance [12]. Time and temperature profiles of the atomization peak can be interchanged depending on the particular analytical application [13,22]. It has been shown that the appearance temperature is dependent upon concentration of the analyte while peak temperature for a specific compound of an element is independent of concentration. The shape of the atomize peak is dependent upon the ramp rate (Figure 1) and for the elements Cd, Zn and Sn a narrower peak is observed with an increasing ramp rate [13,22]. Matousek and Czobik have succeeded in changing the atomization characteristics of Zn, Cd, Pb and Sn by the addition of H_3PO_4 which shifts the peak atomization temperature for these elements to a higher value [10].
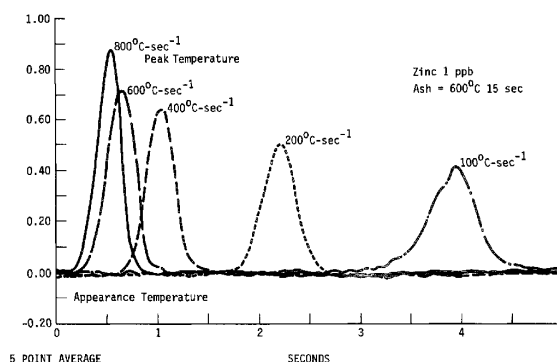

Figure 1.   Change of peak shape with ramp rate.

Practical Application of Matrix Modification

A number of investigations have been carried out on modifying the sample matrix to change the volatilization characteristics of both the analyte and interfering matrix. Most studies have concentrated on the elimination of non-specific absorption resulting from high salt samples such as sea water. Better resolution between the ash and atomize peaks can be achieved by matrix modification, leading not only to more accurate background correction but also as in the case of copper (Figure 2) to an enhancement of absorption signal.
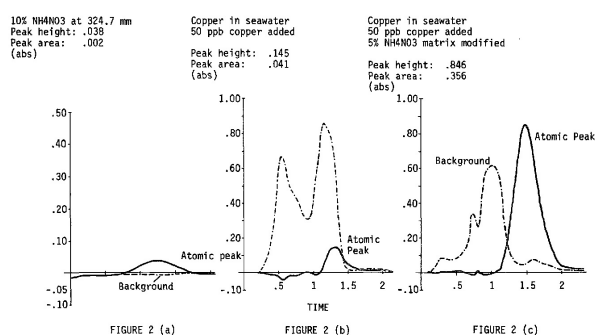

Figure 2.

Frech and Cedergen found that an ash temperature of 1000 °C was required to completely eliminate the non-specific absorption resulting from 2 μL of 2% NaCl [12]. The non-specific absorption resulting from NaCl was found to be reduced significantly (90–100%) at ashing temperatures as low as 500 °C by the addition of ammonium nitrate (1.3 M) or nitric acid (2 M). The proposed mechanisms for the reactions being:

$$NaCl + NH_4NO_3 \rightarrow NaNO_3 + NH_4Cl \text{ and}$$
$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$$
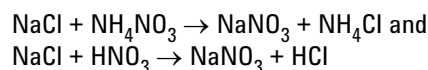
Interference caused by sodium nitrate was completely eliminated by ashing the sample at 615 °C ± 10 °C. In the presence of 2 M nitric acid, lead is not lost at an ashing temperature of 500 °C. To check precision and accuracy, a standard addition calibration was used with additions to a 1:1 mixture of sea water and 4 M nitric acid. This procedure resulted in greater precision and an improvement in the detection limit by about a factor of three.

A further practical tip from the study was that lead was found to be affected by the inert gas flow rate. At a low flow (0.25 L/min argon) a decrease of about 20% compared to a higher flow (4.5 L/min) was observed. This drop in sensitivity was attributed to the formation of gaseous lead oxide at low flows of inert gas. We have found in our laboratories that the analytical curve can vary significantly depending on the inert gas flow. It is therefore wise to incorporate a flow meter and monitor inert gas flows carefully.

Czobik and Matousek have studied chloride interferences occurring in transition metal chloride systems and used phosphoric and suphuric acids as matrix modifiers [11]. The interfering chlorides were converted to the corresponding phosphates and sulphates. Hydrochloric acid which is also formed, is removed during the drying and ashing stages before the atomize signal was generated. The use of phosphoric and sulphuric acids was successful in reducing interferences in the following systems:

$$Pb - CdCl_2, Sn - CdCl_2, Sn - CuCl_2, Sn - CdCl_2,$$
$$Zn - PbCl_2, Zn - CuCl_2 \text{ and } Zn - CdCl_2.$$
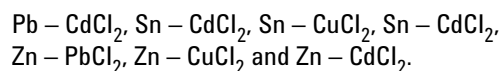
In the $Pb - NaCl$ system, nitric acid proved effective, while the addition of phosphoric acid proved effective in the $Cu - NaCl$ system.

Matrix Modification for Lead and Cadmium in Non-Saline Waters

Thompson, Wagstaff and Wheatstone have investigated ascorbic acid, oxalic acid, ammonium tetramethylene dithiocarbamate, diethylammonium, diethyldithiocarbamate and ammonium nitrate but found them to be unsuccessful for lead and cadmium in non-saline waters [14]. The addition of lanthanum nitrate was found to be successful in reducing the suppression of lead and cadmium signals. Each tube was initially conditioned by the injection (5 μL) of twelve consecutive blanks of 1250 μg/mL of La and a 1% mass/v of 70% nitric acid, while the presence of methane in the purge gas was found to enhance the lifetime of the graphite tube. Prior to analysis of the lead and cadmium the tube was coated with lanthanum nitrate (15 μL of 20% mass/v), carefully dried for 90 seconds, ashed and atomized, a total of three times. This lanthanum coating was considered to be responsible for the change in the volatility of lead.

Reported operating conditions for CRA-90 for 5 μL sample volume [14]:

Lead

Dry	91 °C	50 s
Ash	550 °C	25 s
Atomize	2000 °C	1.8 s Hold
Ramp	500 °C/s	

Inert gas: nitrogen 4 L/min, methane-argon (1 + 9 v/v), 0.20 L/min. Calibration range 2–100 ng/mL.

Cadmium

Dry	91 °C	50 s
Ash	475 °C	25 s
Atomize	2000 °C	1.8 s Hold
Ramp	500 °C/s	

Inert gas: nitrogen 4 L/min, methane-argon (1 + 9 v/v), 0.2 L/min. Calibration range 0.2–10 ng/mL.

Arsenic, Selenium and Boron

Arsenic has been separated and preconcentrated from waste water samples by a diethyldithiocarbamate extraction at pH2 into chloroform after photo-oxidation and analyzed on the carbon rod atomizer [15]. With this method it was possible to investigate a variety of aqueous arsenic species. The total arsenic content was determined after photo-oxidation of the sample with a 450–550 Watt Hg lamp for 3 hours, followed by reduction of the sample to give extractable As[III]. Reduction of the sample is achieved by thiosulphate and bisulphite or metabisulphite in acid solution [23]. Extraction without reduction will give extractable organo arsenic compounds and As[III]. The extractable organo-arsenic compounds can be determined without the addition of the chelating agent diethyldithiocarbamate.

Recoveries of 103% ± 6.4% were obtained after both oxidation, reduction, and extraction using the chelating agent.

A similar scheme could also be devised for the analysis of selenium [16] which can be extracted as (Se^{IV}) by diethyldithiocarbamate at pH4–6 in carbon tetrachloride [22]. Total selenium has been determined in raw sewage and primary effluents after a nitric-perchloric acid digestion [17]. The sample treatment involved 500 mL of waste water, 5 mL of nitric acid, 2 mL of 20% perchloric acid boiled gently on a hot plate until all organic matter was digested, with the final volume of the sample being 50 mL. The concentration factor was therefore 10. An average of 88% recovery was obtained and no interference from Al, Cr, Cu, Mn, Ni and Zn in 1000 fold excess, Fe and Mo in 600-fold excess and Pb, Bi, V in a 150-fold excess was observed at the 196 nm resonance line for Se. The halide salts of K and Na at 1000 mg/L level produced significant background which was observed by monitoring the 198.1 nm non-absorbing line. Raw sewage gave a lower recovery of selenium as primary effluent which was attributed to adsorption on the suspended material. A reduction in sensitivity of 25% in peak height was evident due to the presence of perchloric acid which was overcome by the further addition of nitric acid.

Boron is necessary for plant growth because it plays an important role in the formation of pectic substances in plant cell walls and is an essential constituent in the carbohydrate and nitrogen metabolism. Boron can have deleterious effects in concentrations above 2 µg/mL in water. Analyzed by CRA-90, the characteristic concentration for boron is reported as 6 ng/mL [18]. The mean value for boron in a certified orchard leaf sample (33 ± 3 µg/g) was found to be 35.1 µg/g.

Matrix Modification of Arsenic, Selenium and Boron Samples

The addition of a twenty-fold excess of nickel or cobalt to arsenic or selenium samples has markedly improved both the sensitivity and atomization characteristics of arsenic and selenium due to the formation of stable nickel and cobalt selenides and arsenides [19]. In the case of arsenic a twenty-fold excess of nickel or cobalt added to the graphite tube prior to analysis has lead to a two-fold improvement in sensitivity and the possibility of using an ashing temperature of 1000 °C without loss of arsenic. For selenium a twenty times excess of nickel or cobalt improves sensitivity by about 30% and permits an ashing temperature up to about 1000 °C without loss, whereas selenium is lost above 200 °C in the absence of nickel. Other possible matrix modifying agents for arsenic (Cu, Pt, Fe, Mn, Pt) and selenium (Ba, Cu, Fe, Mn, Mg, Zn) were investigated but these gave no appreciable change

in signal characteristics. The addition of nickel to the sample also eliminated interferences resulting from a ten-fold excess of selenium on arsenic (70% loss of As signal) and ten-fold excess of arsenic on selenium (50% loss in Se signal).

A series of elements that form borides (Ba, Ca, Ce, Cr, Mg, Sr) have been investigated in an effort to maximize enhancement of boron's signal [18]. Barium hydroxide has been found to be superior when present at 1000 µg/mL.

Table 1.   Summary of Analytical Conditions for Arsenic, Selenium & Boron on CRA-90

Arsenic	5 µg volume	
Dry	100 °C	35 s
Ash	1000 °C	10 s
Atomize	2100 °C	3 s Hold
Ramp rate	600 °C/s	
Inert gas	N$_2$ or Ar	
Matrix modification		
20-fold excess of nickel or cobalt applied directly to CRA tube (5 µL, 20 µg/mL Ni).		
Selenium	**5 µg volume**	
Dry	100 °C	35 s
Ash	600 °C	20 s
Atomize	2100 °C	2 s Hold
Ramp rate	600 °C/s	
Inert gas	N$_2$ or Ar	
Matrix modification		
20-fold excess of nickel or cobalt applied directly to CRA tube (5 µL, 20 µg/mL Ni).		
Boron	**5 µg volume**	
Dry	100 °C	35 s
Ash	1100 °C	25 s
Atomize	2600 °C	3 s Hold
Ramp rate	600 °C/s	
Inert gas	Ar or H$_2$	
Matrix modification		
1000 µg/mL barium hydroxide in sample [18].		

Further methods of analysis of water samples are contained in C. W. Fuller's monograph on Electrothermal Atomization [20].

Detection of Organic Pollutants in Water by Vapor-Phase Absorption Spectrometry using a CRA-90

The UV absorption spectra arising from the evaporation or thermal pyrolysis of organic substances in a nitrogen atmosphere has been used as a fingerprint for organic pollutants [21]. Compounds which include petroleum products, cooking oils, detergents and various fatty acids have been investigated using a CRA-90 with a slow ramp rate (11 °C/s – 50 °C/s) from 0 °C to 1750 °C. As samples are heated, the absorbance is measured at any of the following wavelengths: 190, 210 and

253.7 nm. The resultant spectra are traced on a chart recorder. The technique which is rapid and sensitive has been used to characterize pollutants, screen samples for organic substances such as non-ionic detergents, and as an indicator for setting up gas chromatography conditions.

Sample Preparation for Organic Pollutants in Water

An aqueous sample is extracted into either hexane or chloroform and a small aliquot (0.1–10 µL) injected onto the carbon tube. The solvent is dried (hexane 35 °C 20 s; chloroform 65 °C for 30 s) and ramp applied to the tube, to a maximum atomize temperature of 1750 °C while the ashing parameters were set to a minimum.

In summary, furnace atomization is an extremely sensitive microanalytical technique capable of determining many trace elements without pre-concentration in water at the µg/mL level. It is therefore essential that instrumental conditions be optimized and due care taken to minimize non-specific absorption using a technique such as matrix modification. When dealing with trace elements at low levels good laboratory practices must be followed. Contamination from reagents, storage containers and analytical equipment used in sample treatment significantly affects the precision and accuracy of results. The use of reagent blanks and the cleaning of analytical equipment can reduce errors arising from contamination. Bruland et al. have covered this area extensively [4].

The chemical analysis of water is a large field, and in-depth methods using the carbon rod are available [1, 24–26]. These should be consulted if a water quality program is to be implemented for compliance with national regulations.

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